Carbon Dioxide Removal from Flue Gas Using Microporous Metal Organic Frameworks (MOFs)

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24 March 2009

NETL CO_2 Capture Technology for Existing Plants R&D Meeting
DE-FC26-07NT43092

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UOP Overview

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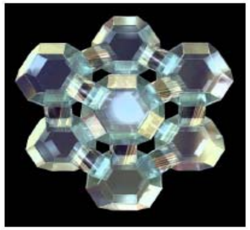
Business Units

Catalysts, Adsorbents & Specialties	Process Technology & Equipment	Renewable Energy & Chemicals
CA&S	**PT&E**	**RE&C**

- **Develop & deliver innovative technologies**
- **Design, engineer, license & service process technology**
- **Manufacture catalysts, molecular sieves, adsorbents & specialty catalytic products equipment**
- **Provide consulting services for the optimization & technical management for the hydrocarbon industry**
- **Solve problems with technology & transfer that technology to customers**

Technology Licensing

Performance Improvement Partner



Leading Supplier of Catalysts & Molecular Sieve Adsorbents

Project Overview

Funding Highlights and Dates

Total budget: $2,802,200

- DOE/NETL share = $2,230,672
- UOP share = $571,528

2 April 2007 to 31 March 2010

Project Organization

DOE/ NETL Project Manager
David Lang

Organic chemicals advisor
HON Specialty Materials

Energy partner advisor
EPRI

UOP Project Manager
UOP Principal Investigator
Rich Willis

University of Michigan
Prof Adam Matzger

University of Edinburgh
Prof Stefano Brandani

Northwestern University
Prof Randy Snurr

Vanderbilt University
Prof Douglas LeVan

Others at UOP
Annabelle Benin
John Low
Ganesh Venimadhavan
Paulina Jakubczak
Syed Faheem

Our Collaborative Approach

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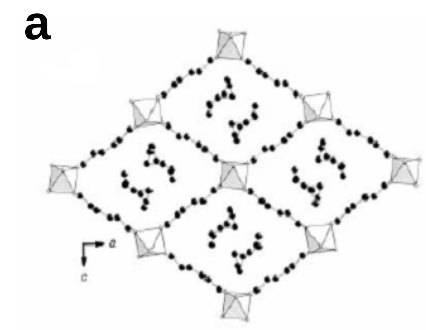
- **Make MOF Materials**
  - **Team ideas** ***UM and UOP***
  - **Literature compounds**

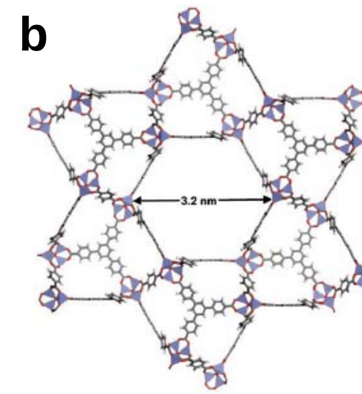
    a) MIL-53 from Ferey, et al, *JACS* 2002, *124*, 13519.

    b) UMCM-1 from Koh, et al, *ACIE* 2008, *47*, 677.

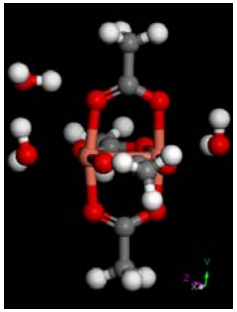
a

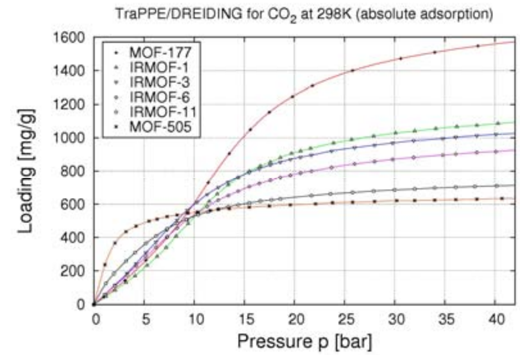


b



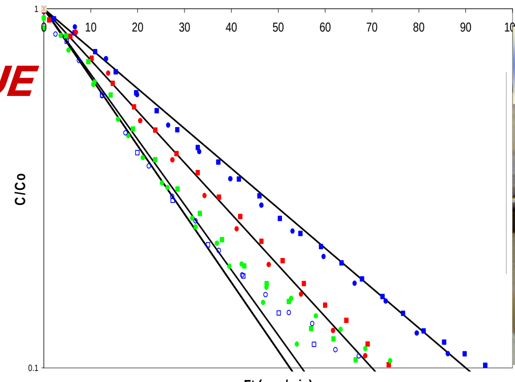
- **Model Interesting Materials**
  - **Hydrolysis** ***UOP***
  - **Isotherms** ***NU***
  - **Maximum theoretical surface areas**

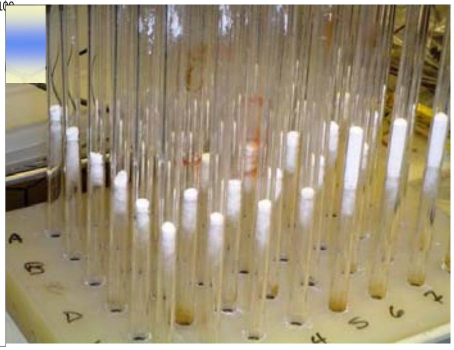




HKUST-1 from Williams, et al, *Science* 1999, *283*, 1148

- **Evaluate materials**
  - **Adsorptive properties** ***VU and UE***
  - **Hydrothermal stability** ***UOP***





Overall Objectives and Scope

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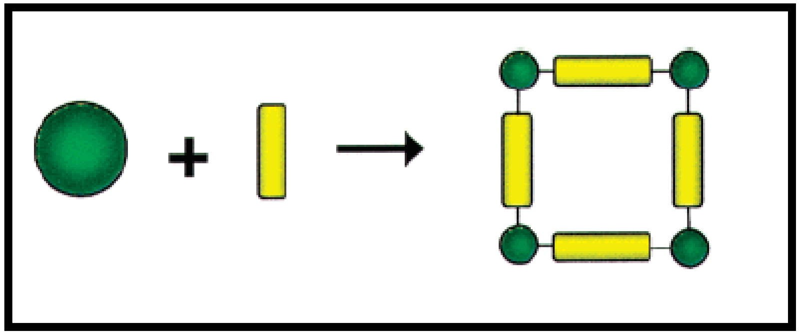
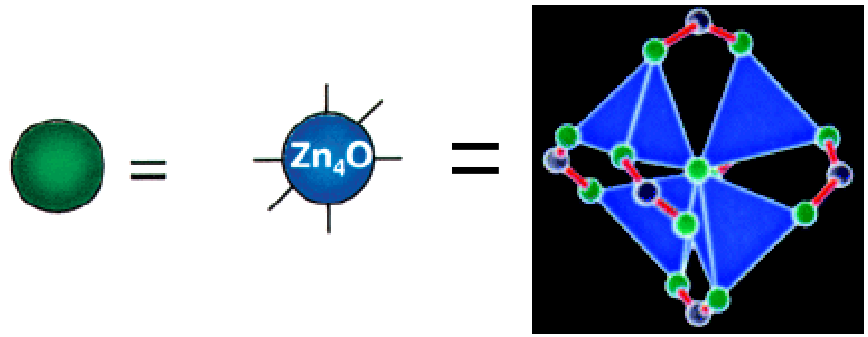
- Develop a MOF-based CO_2 capture process
- Design a pilot study to evaluate process:
  - performance
  - economics

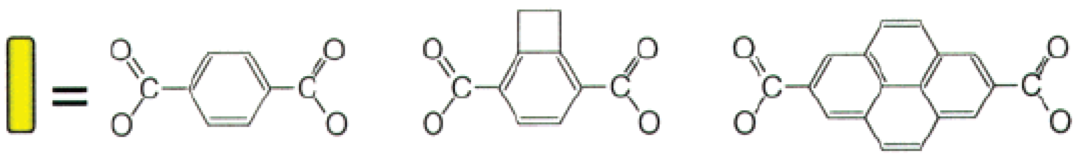
- Year 1 *(ended 31 March 2008)*
  - synthesize and screen up to 50 MOFs
  - evaluate and establish baseline adsorption equilibrium characteristics for MOFs in general
- Year 2 *(ends 31 March 2009)*
  - down-select to ~10 best candidate MOFs to optimize
  - determine water and other contaminant effects
  - begin scale-up and forming
- Year 3 *(ends 31 March 2010)*
  - further optimize one or two MOFs
  - determine adsorption kinetics
  - develop process design and economics analyses

Technology Fundamentals/ Background

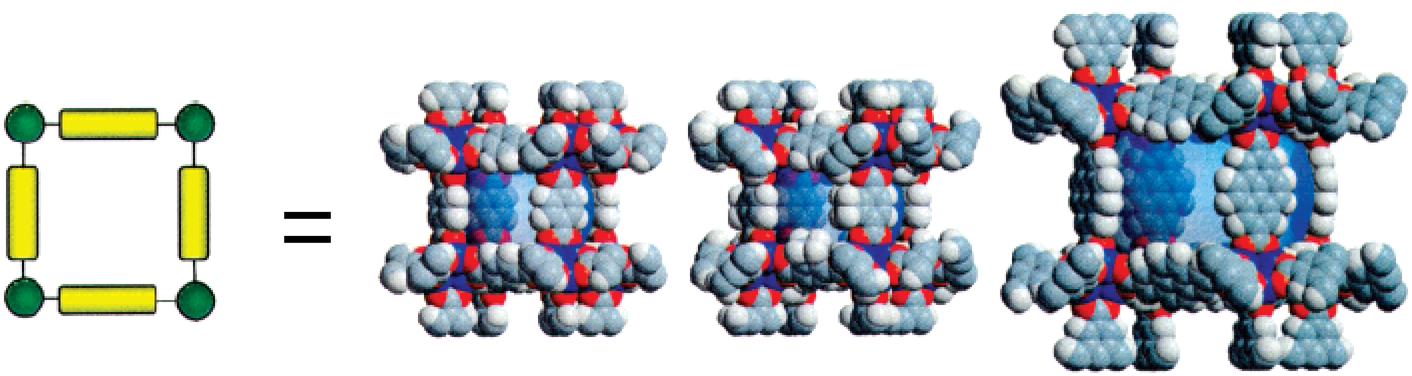
MOF construction







IRMOF-1 IRMOF-6 IRMOF-14

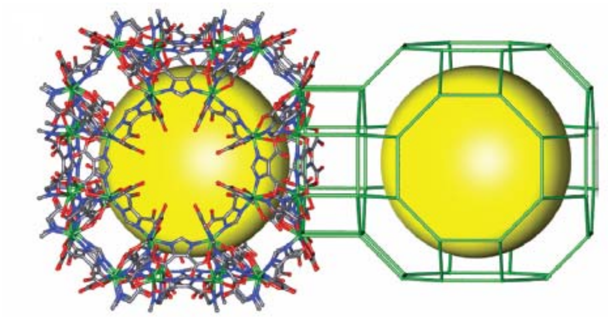


some graphics from Yaghi, et al, Nature, 423 (2003) 705

Properties: Zeolite versus MOF

similarities to zeolites:

- synthesis conditions
- good yields
- crystalline
- tunable hydrophil(phob)icity and acid(basic)ity

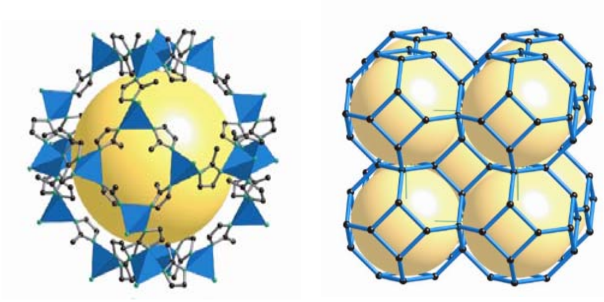


rho

ZMOF-rho from Eddaoudi, et al, *Chem Comm* 2006, 1488

differences from zeolites

- lower temp stability (up to 450 ºC reported)
- much higher SA and PV per gram
- more unobstructed gas diffusion
- much more diverse chemistry
    - many more metals/ metal clusters available
    - organic linkers can contain functionality



sod

ZIF-8 from Yaghi, et al, *PNAS* 2006, *103*, 10186

material	surface area, sq m/g	crystal density, g/cc	% free volume	pore size, Å	stability, deg C	CO2 heat adsorp, kJ/mol
NaX	700	1.44	49	7.4	> 700	50
IRMOF-1	3800	0.62	79	12	400	15

PSA Technology Fundamentals

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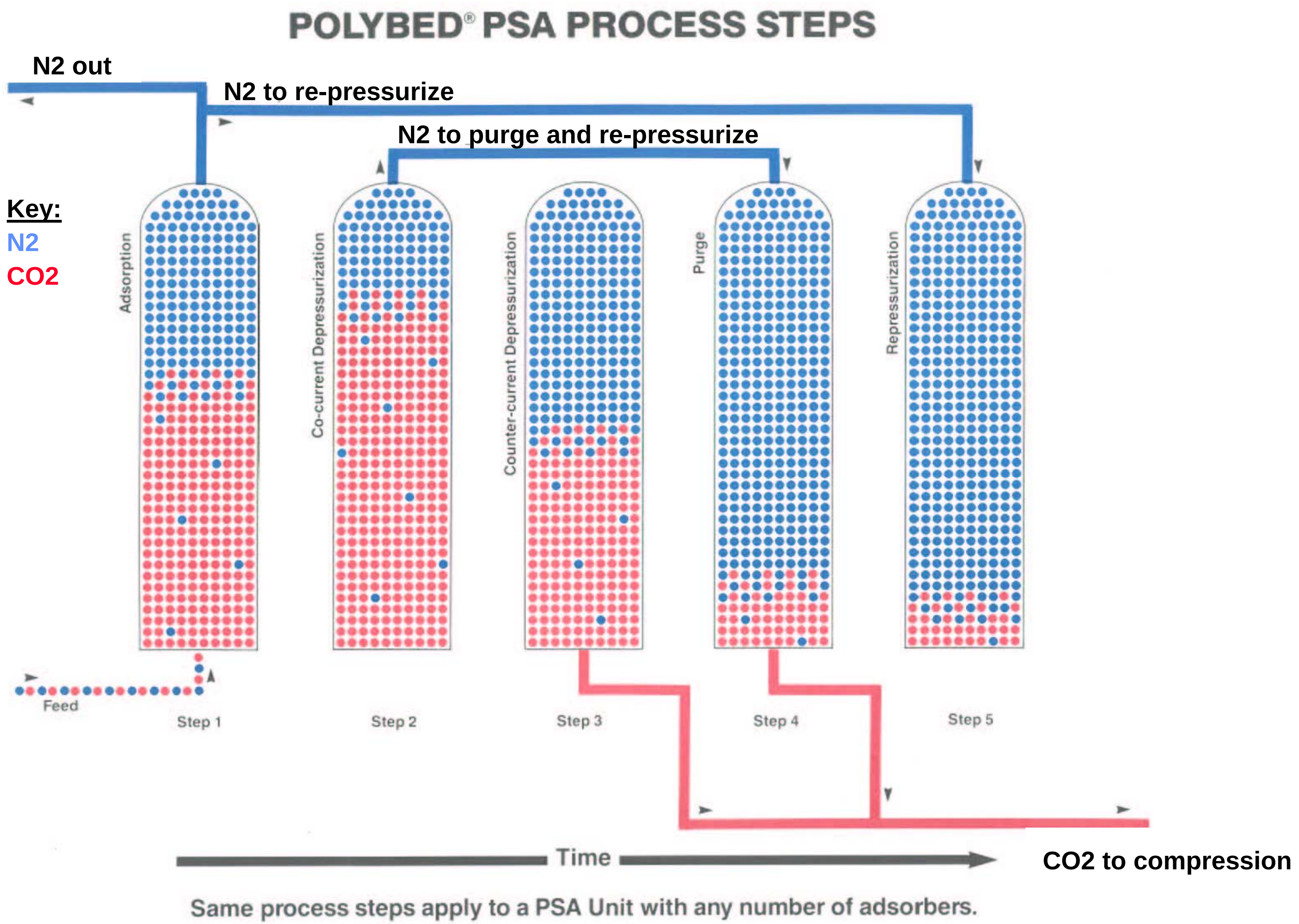
Utilize MOFs in a Pressure Swing Adsorption (PSA) process to remove CO_2 from coal-fired power plant flue gas

- **Vacuum PSA system with multiple beds and five basic steps**
  - adsorption, co-current depressurization, counter current depressurization, purge and re-pressurization carried out according to a complex algorithm

- **Feed T = 100 - 120 ^{o}F**
- **Feed P = 19 psia**
- **Pressure of CO_2 to compression= 0.5 psia**
- **Temperature of CO_2 to compression= 100 - 120 ^{o}F**

Schematic of the PSA process



Technical and Economic Advantages

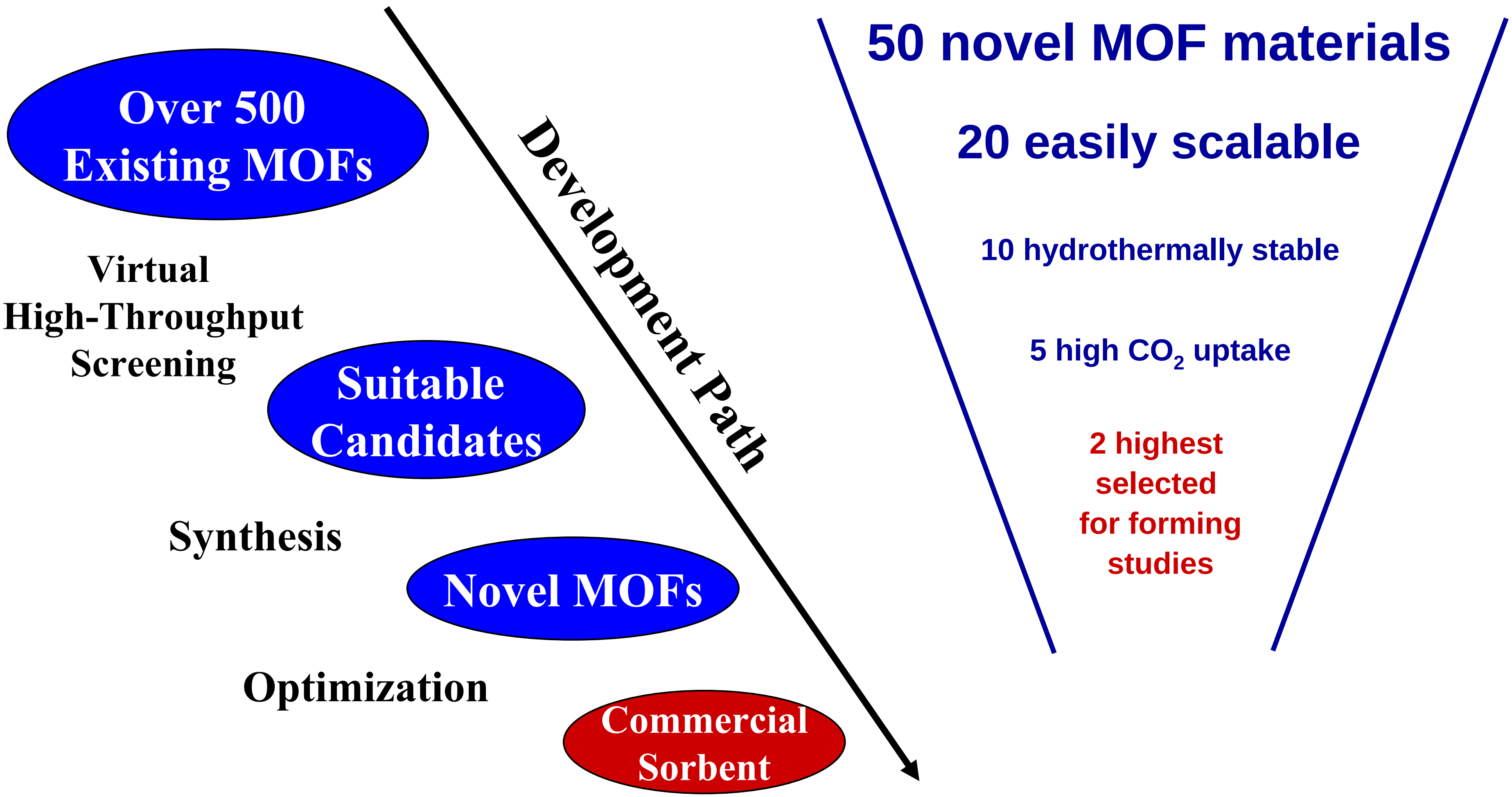
- **Environmentally friendly**
- **Less parasitic power required for the capture process**
  - However, higher compression power required to compress up from the sub-atmospheric VPSA outlet to pipeline pressure

Technical and Economic Challenges

- **Effect of steam, SOx and NOx on the MOF material**
- **Selectivity for CO_2 over Nitrogen**
  - Amount of N_2 that needs to be compressed along with the CO_2
  - The necessity for separating N_2 from CO_2 before further compression and transport
- **Large vacuum pumps to compress the CO_2 from the outlet of the VPSA**
- **Pressure drop across the VPSA beds**

Progress and Current Status

Down-selection Process



Progress and Current Status

Key MOF Properties	**Status 31 Dec 2008**
high adsorption capacity	*so far, so good*
easily regenerable	*so far, so good*
good adsorption/ desorption rates	*OK unless pores small*
high selectivity	*especially CO_2 over nitrogen and water*
stable to O_2, SOx, NOx	in progress

Equipment

Combinatorial Heat Treatment Unit (HTU)

Max T	900 °C
Max steam	50 %
# of Steam conditions	6
Max flow	400 ml/min
Max loading	~2 mL max loading
Physical	48 Quartz reactors 48 temp controls 6 independent pumps Gas blending downflow
Software	Controls pumps and collects flow data Controls blending system and collects data

Equipment

Semi-Automated Zero Length Column (ZLC)

T range	30 - 400 °C
P range	(atmospheric) P_{CO2} in He 0.001 – 0.1 bar
Sample size (equilibrium)	10 – 15mg
Sample size (kinetic)	1 – 3mg
Sample size (breakthrough)	gram
Software	Labview control (semi-automated)

DID detector (long time decay for desorption)
TCD detector (for CO_2)
Mass Spec detector (binary data)
High speed mass flow controllers

Equipment

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Rubotherm

T range (regen)	600 °C
T range (test)	10 – 400 °C
P range (test)	2 torr – 100 bar
Vacuum	1 x 10^{-3} torr
Weigh accuracy	+/- 1.0 μg
Sample size	70 – 90mg

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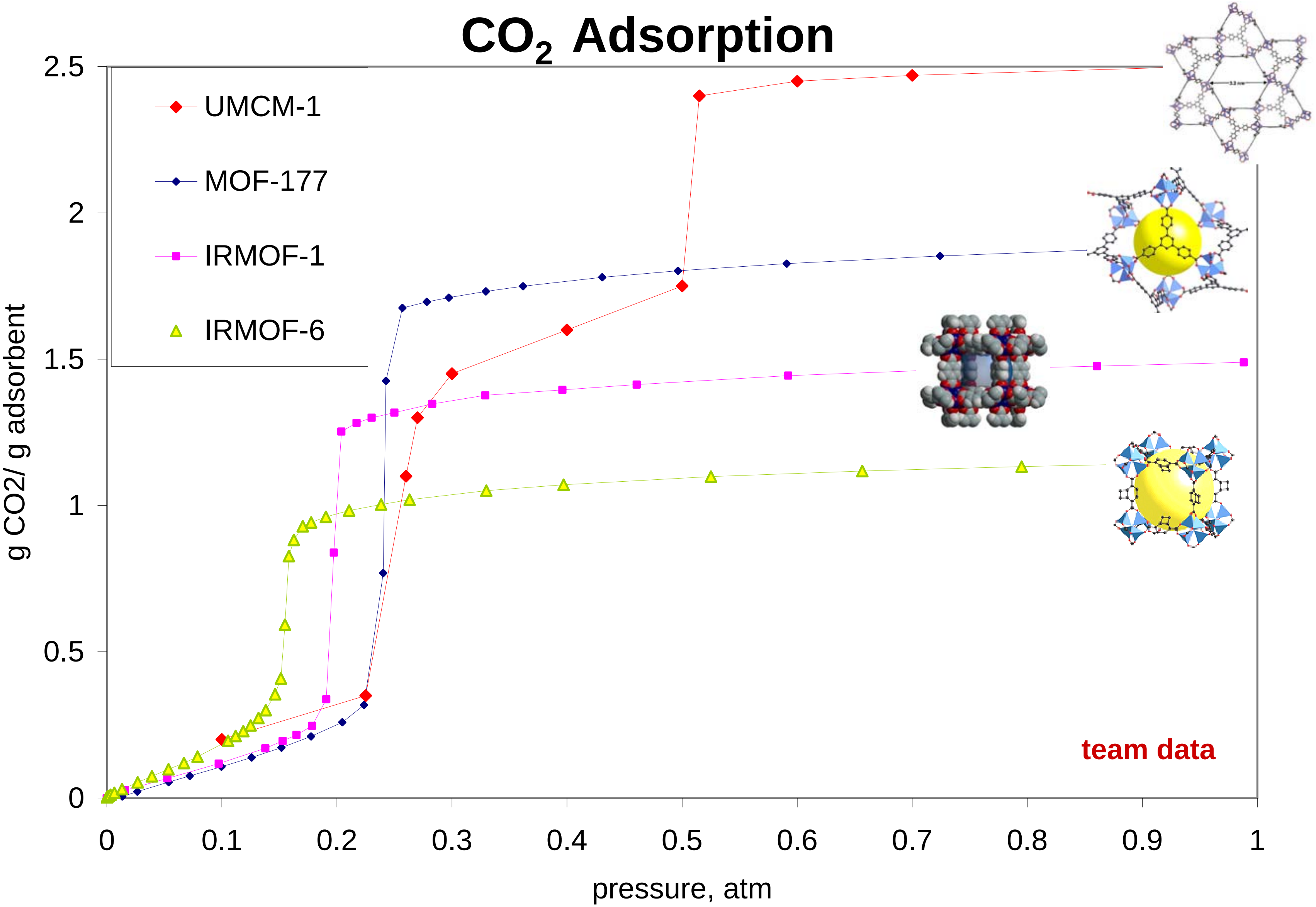
Supernanoporous MOFs at 195K



unfortunately, 195K performance is not predictive for 298K

HKUST-1: Ambient to High Temperature

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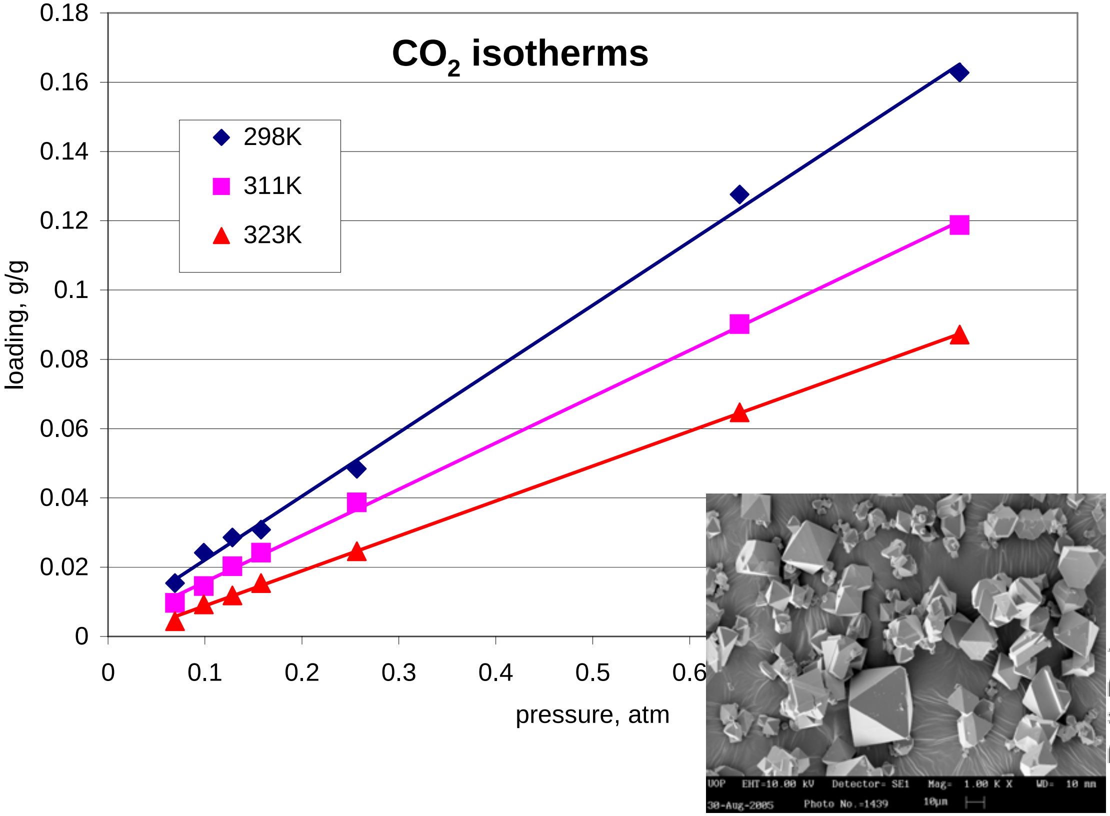

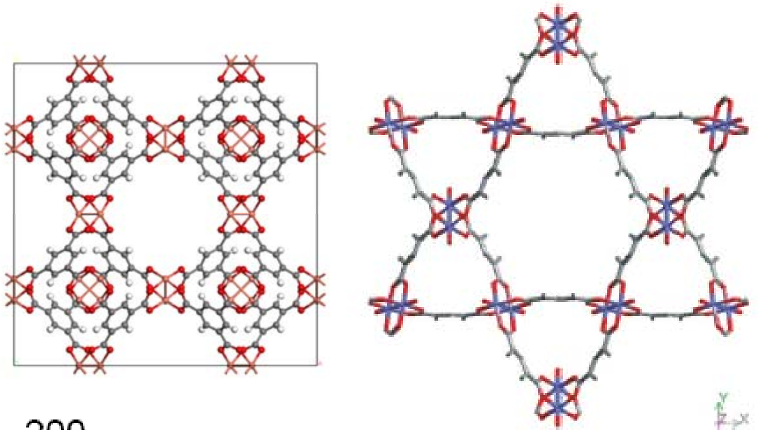

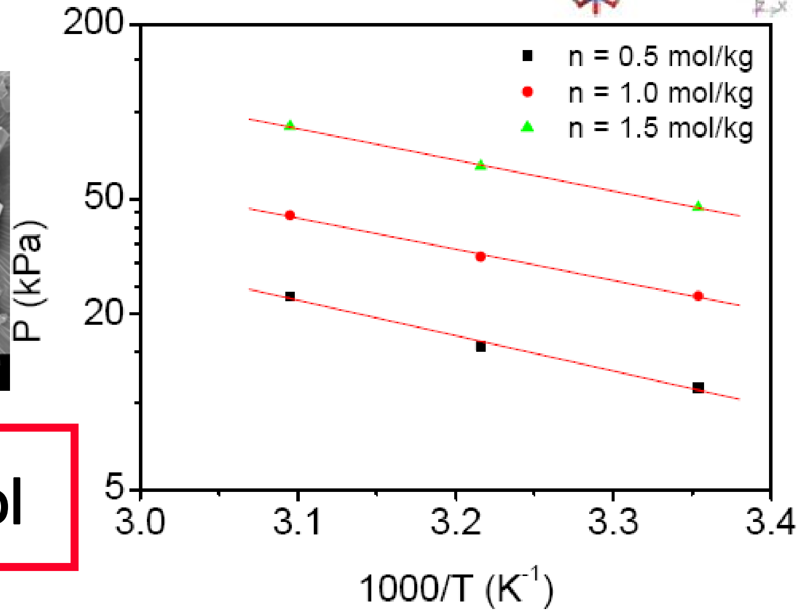

q_{st} of CO_2 on HKUST-1 : 23 ± 1 kJ/mol

$$\ln(P) = \frac{-\Delta_{vap} H}{nR}\left(\frac{1}{T}\right)$$

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Case Study: ZIF-8

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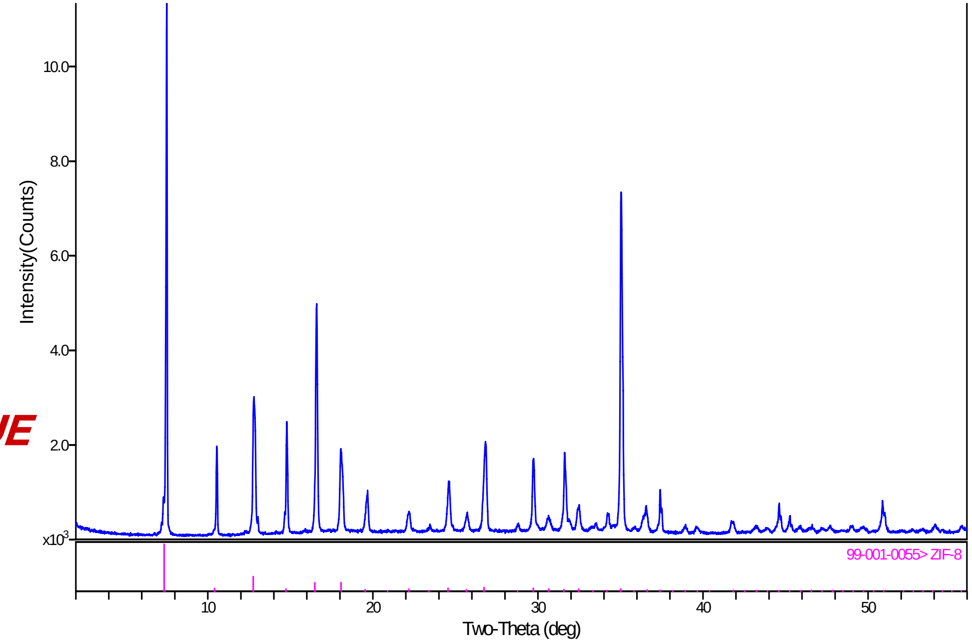
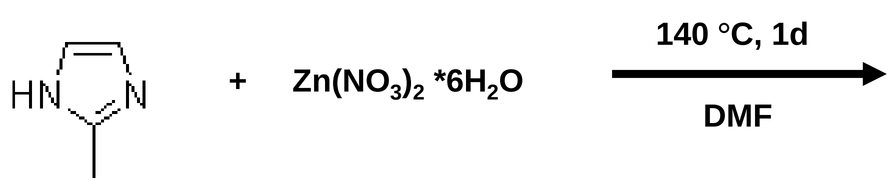
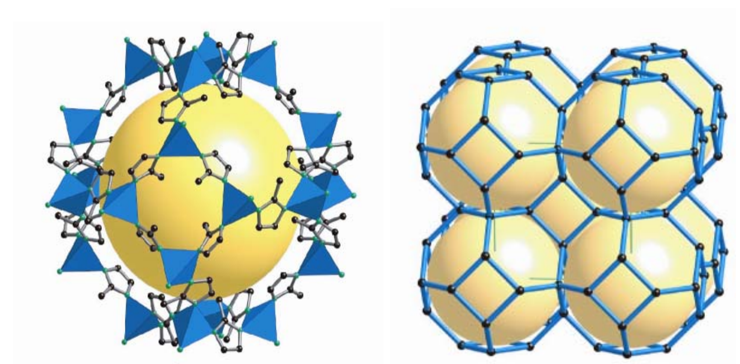
- **Make it** ***UOP***
- **Model it**
  - **Isotherm** ***NU***
  - **Hydrolysis** ***UOP***
- **Evaluate it**
  - **Adsorptive properties** ***VU and UE***
  - **Hydrothermal stability** ***UOP***

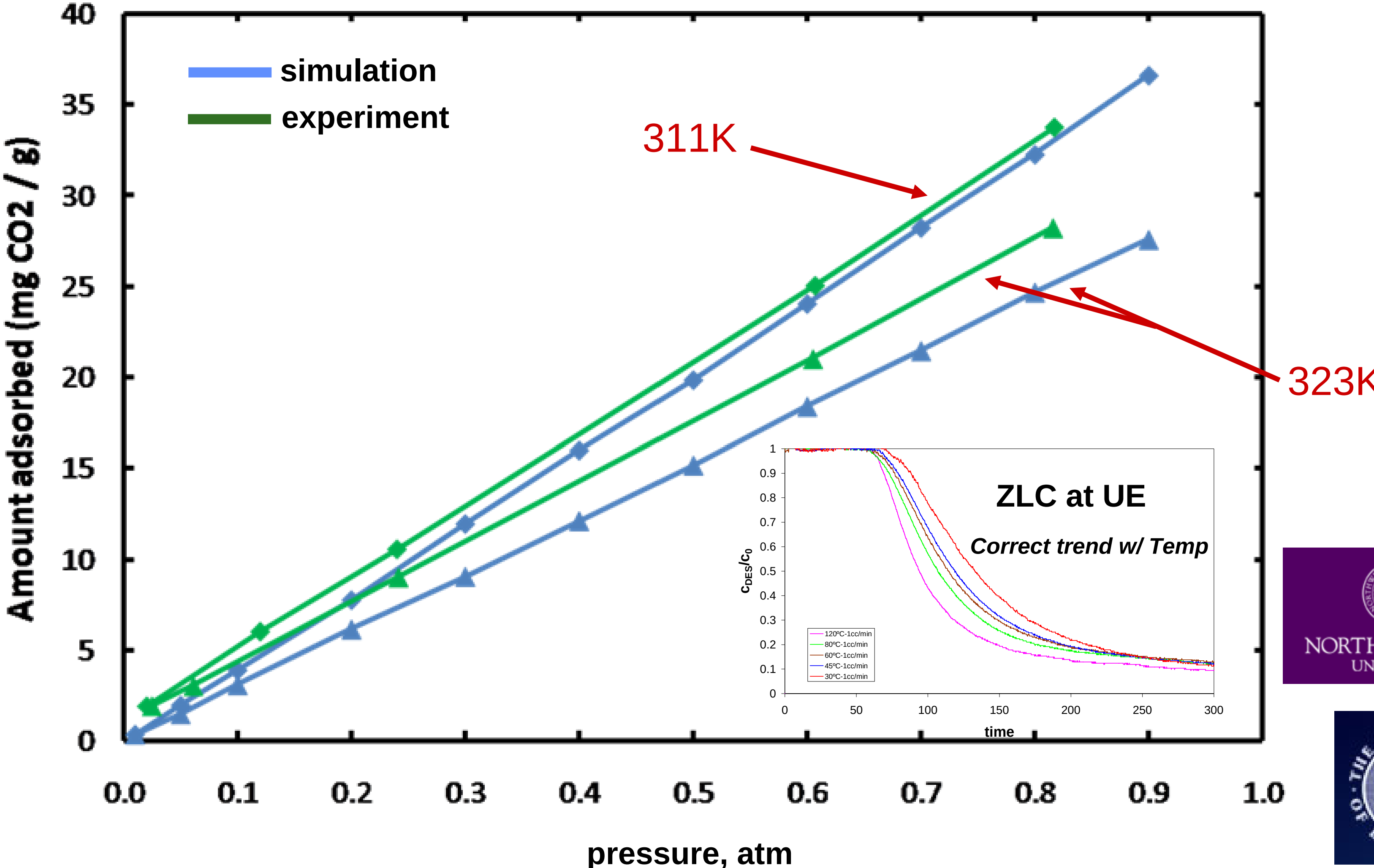






Yaghi et al, *PNAS* 2006, *103(27)*, 10186-10191.

ZIF-8: CO_2 Isotherm Model Matches Experiment



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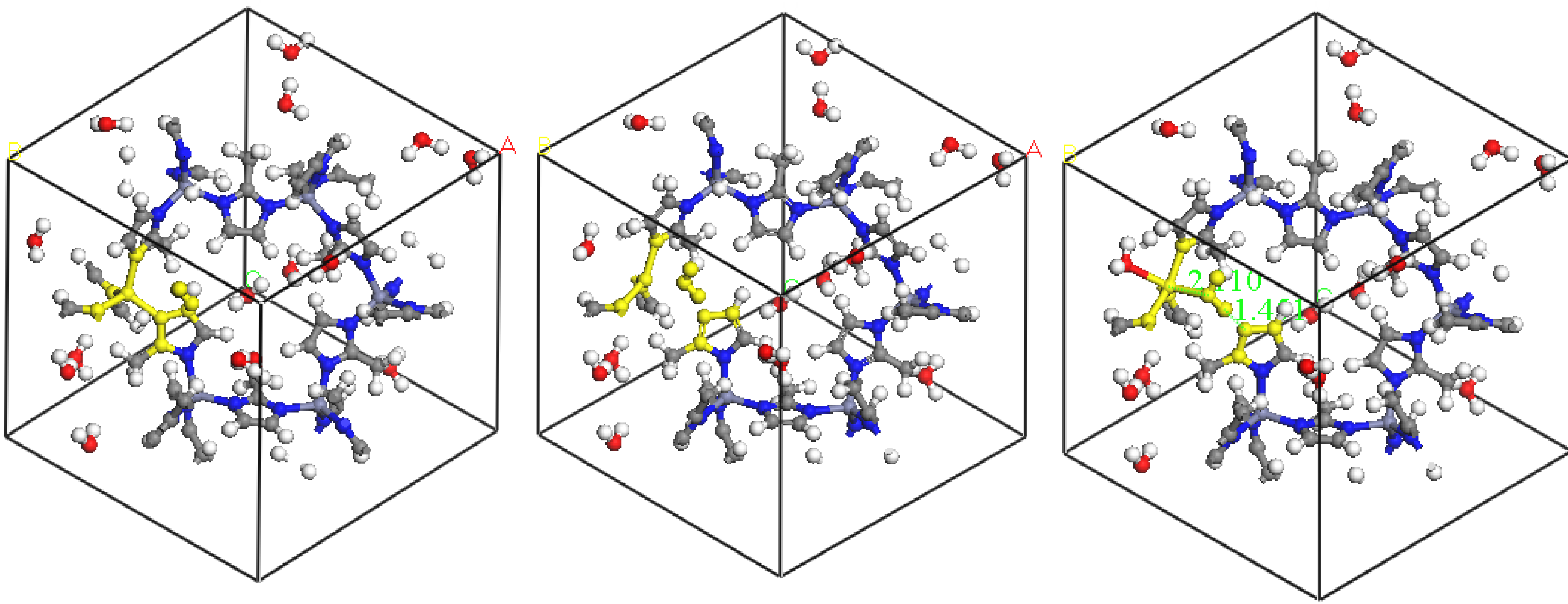
CO_2 adsorption experiment and simulation match

ZIF-8: Model Predicts Hydrothermal Stability



E of transition state: 55.7 kcal/mol

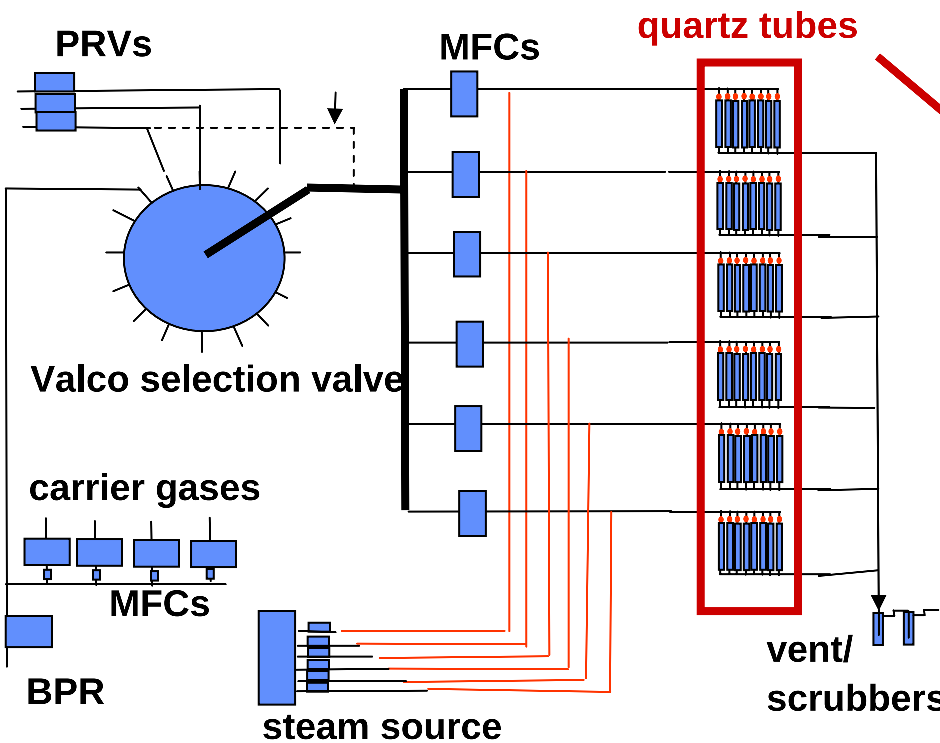
Zn-N bond broken

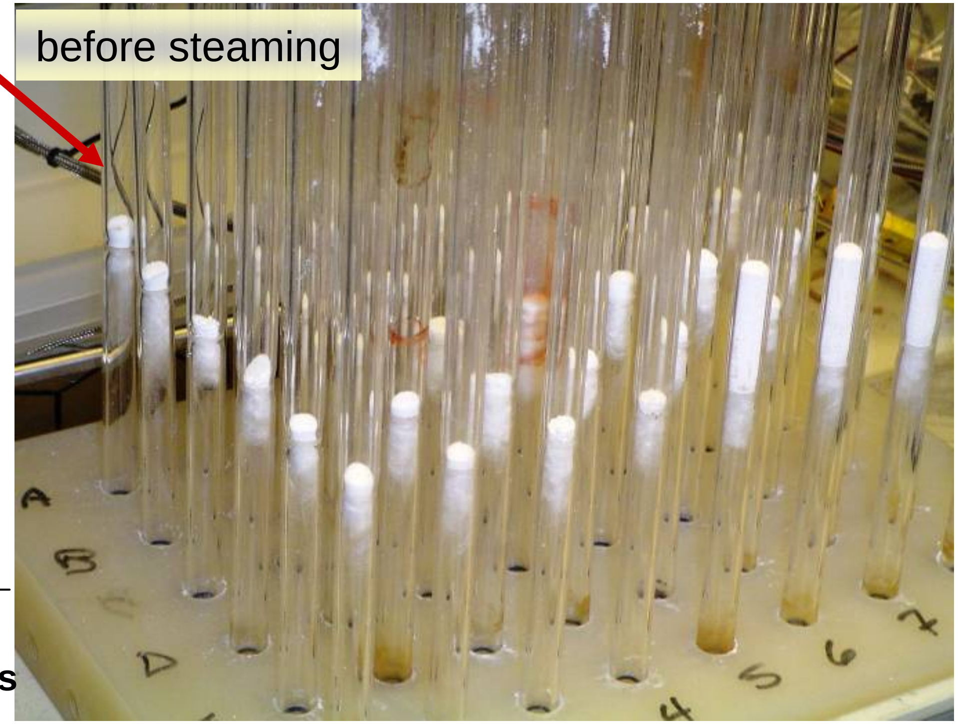
Zn-O bond forms

E of rxn : 22.7 kcal/mol

<u>prediction:</u> very hydrothermally stable

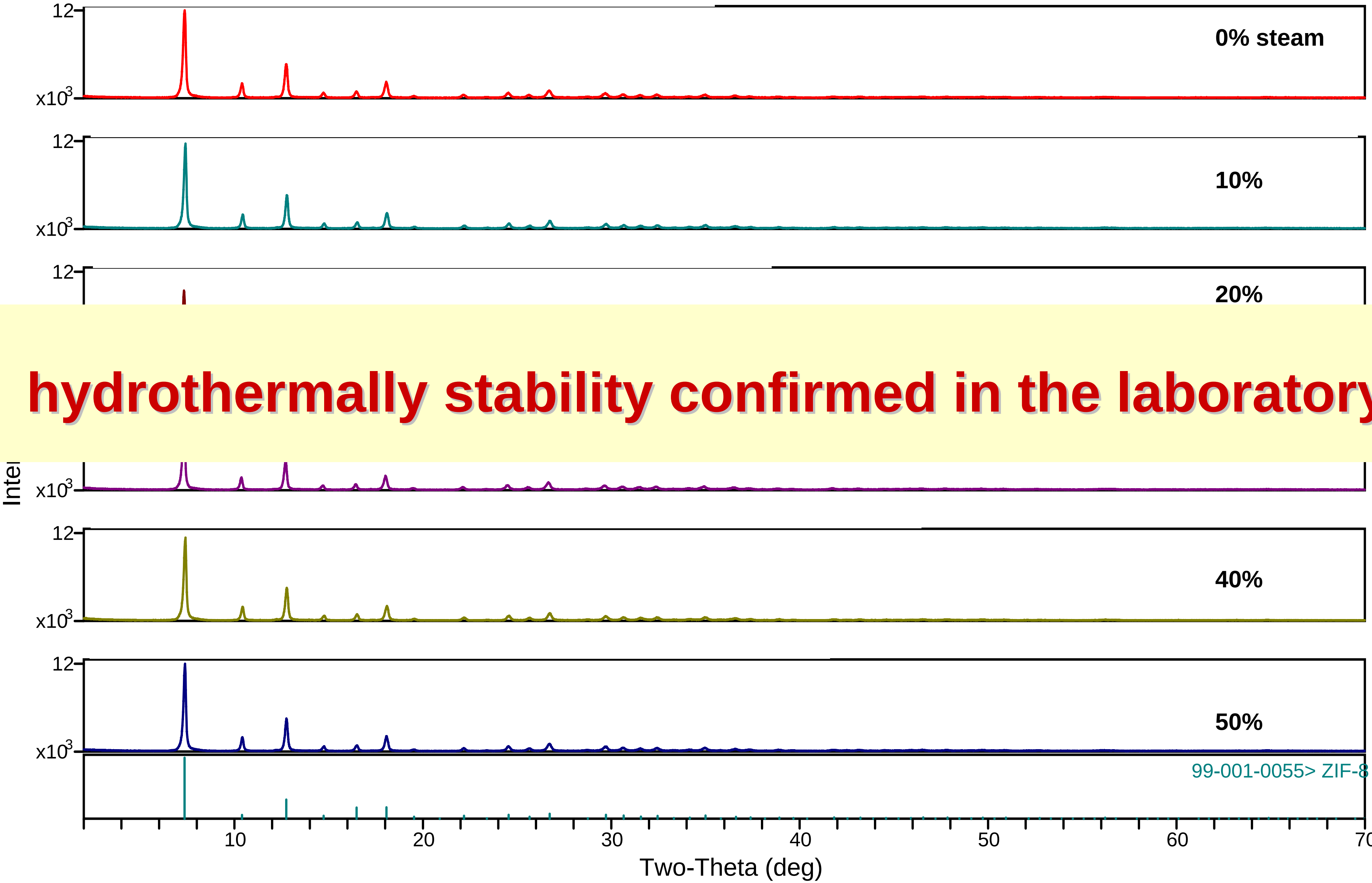
High-Throughput Hydrothermal Stability Testing





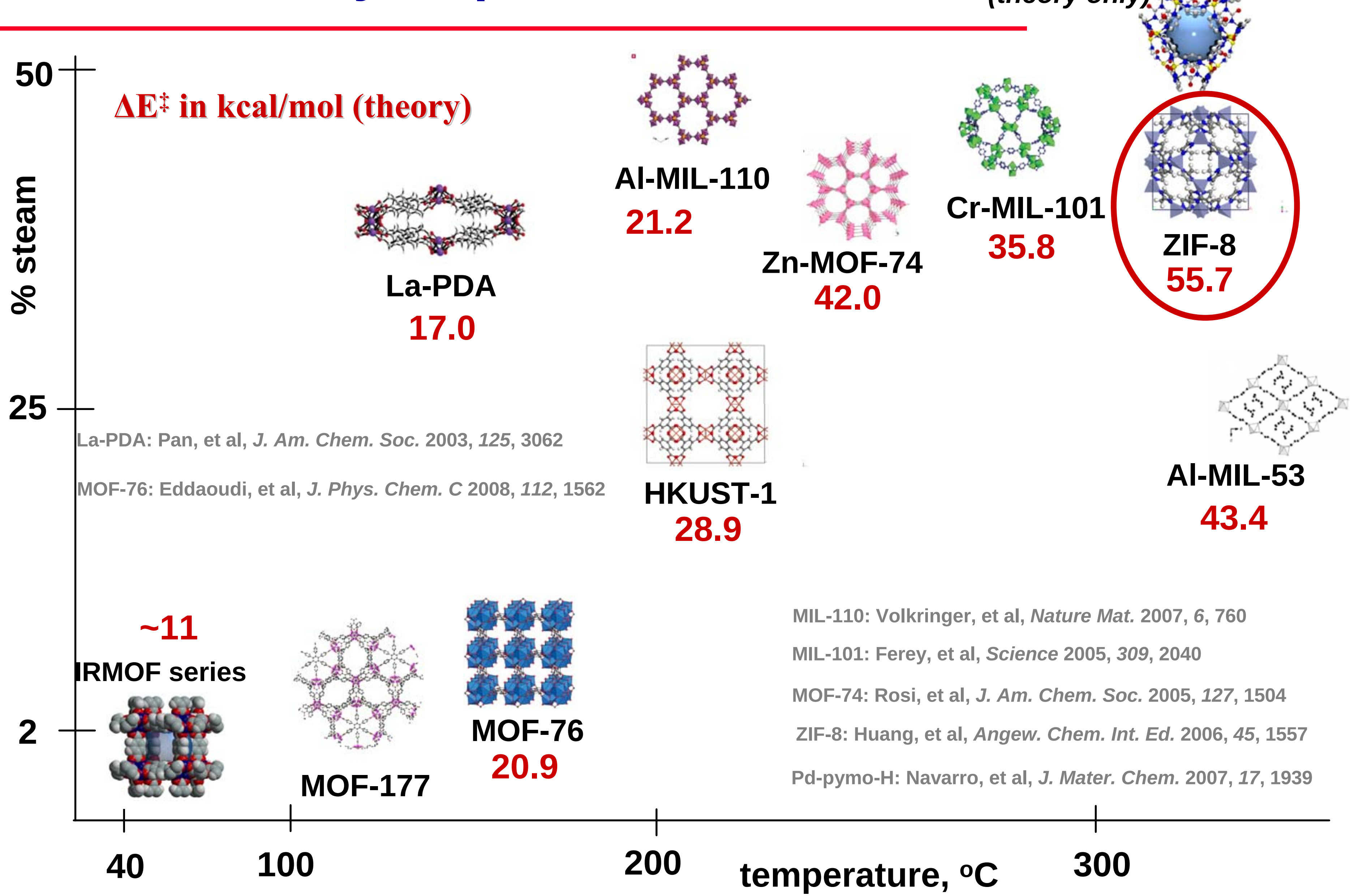
<u>As-synthesized samples:</u>
solvent exchanged
dried (elevated temp)
loaded
activated (elevated temp) in N_2 overnight
steam 0 - 50%, 40 - 400C, 2 hours
unload in air, XRD in air

ZIF-8: 300 °C Treatment for Two Hours



hydrothermally stability confirmed in the laboratory

Steam Stability Map



Summary and Path Forward

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Summary

- A wide variety of MOF materials successfully synthesized and evaluated
- Theory correlates well with experimental results
  - Experimental and simulated isotherms match nicely
  - Hydrothermal stability predictions trend with steaming studies
  - ***Recent results helping guide experiments***
- Progress has been made on CO_2 Capture with MOFs
  - Team hitting on all cylinders

Path forward

- Collect more CO_2 data in moisture-containing streams
- Begin contaminant (NOx, SOx etc.) testing
- Explore new synthesis space

Success Criteria Summary

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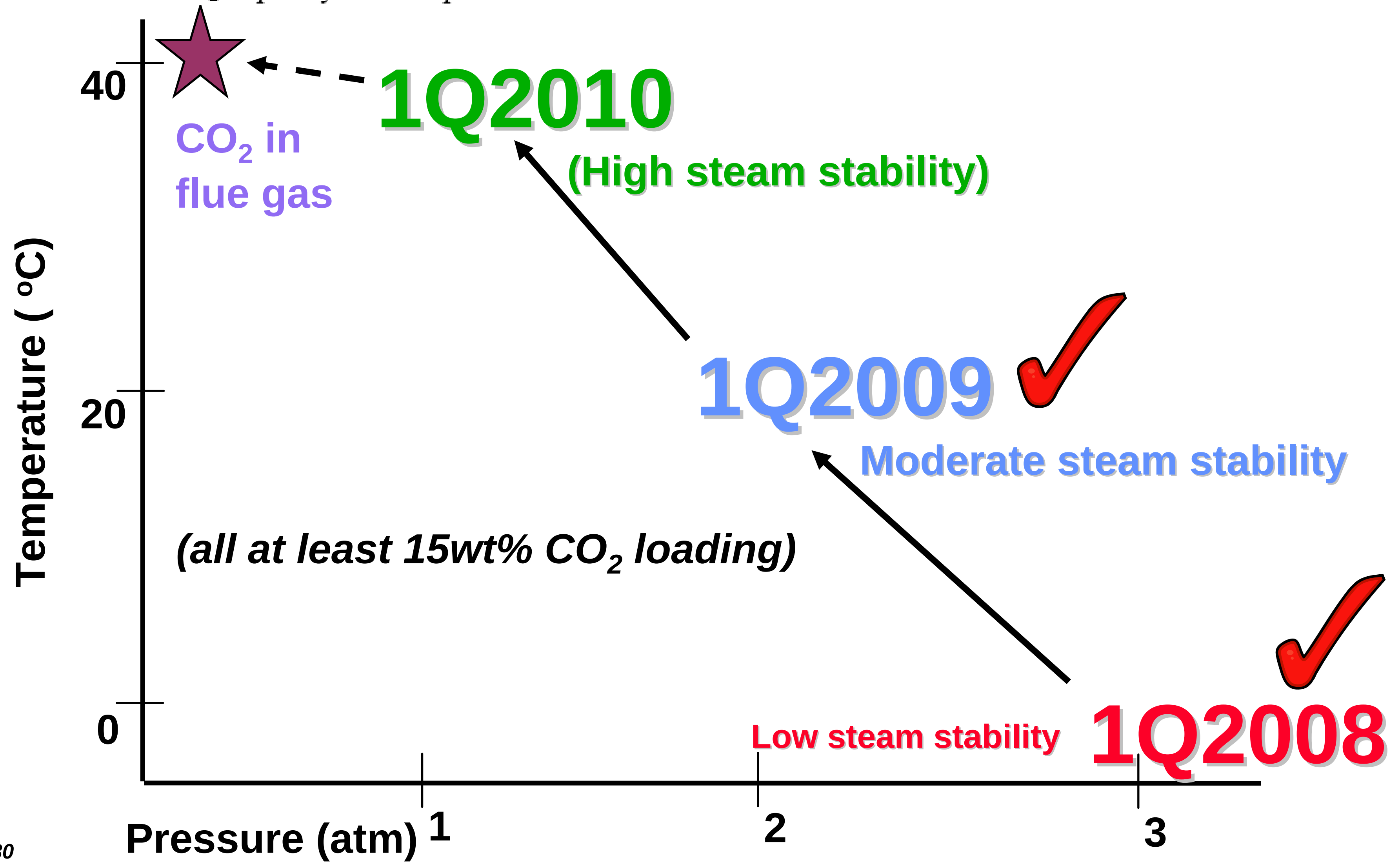
Moderate steam stability End of Phase II performance targets are 15 wt% CO_2 capacity at 20 °C at up to 2 atmospheres pressure. A minimum stability target will be retention of 75% CO_2 capacity after exposure of material to 3-7 mole% steam at 100 °C for 2 hours.



Plans for the Future: Testing

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<u>Phase III Objective:</u>

Demonstrate one or more MOF materials that meet performance targets and have sufficient stability to carry into pilot testing

<u>Phase III Performance Targets:</u>

15 wt% CO_2 capacity at 40 ^{o}C at up to 1.25 atm pressure

> <u>Minimum Stability Target:</u>
>
> Retention of 75% CO_2 capacity after exposure up to 15 mole% steam at 150 ^{o}C for up to 24 hours

Ends 1 April 2010

Plans for Future: Development and Commercialization

- (A) A MOF optimized for flue gas ✓
  - Meets material performance targets for CO_2 removal
  - Synthesized in sufficient quantity to support a pilot study
- **(B) Commercialization study report** ✓
- **(C) Process design report**
  - Design details for a CO_2 removal from flue gas process using the optimized MOF
  - Pretreatment requirements and process conditions included
- **(D) Pilot study design report**
  - Design details for a two-stage pilot study comprising:
    - Preliminary pilot study in stand-alone pilot plant
    - Field study operating on slipstream from an operational plant
- **(E) Economic design report**
  - Detail on the inputs, assumptions and results of estimating the costs and energy requirements for a commercial scale CO_2 separation unit using the MOF-based adsorption process

Acknowledgements

This project is supported by the U.S. Department of Energy through the National Energy Technology Laboratory, under Award No. DE-FC26-07NT43092. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of the DOE.

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